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Singlet state photochemistry of dibenzyl ketone and its *o*-tolyl derivatives

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Abstract

The singlet state contribution of α -cleavage in the photochemistry of dibenzyl ketone (DBK) and *o*-tolylmethyl benzyl ketone (TBK) was investigated. The fitting of a master Stern–Volmer equation for the simultaneous quenching of the S_1 and T_1 states of DBK and TBK leads to the conclusion that in both ketones α -cleavage occurs in the singlet state, but to a lesser (20%–30%) extent than in the triplet. Comparison of the relative fluorescence and α -cleavage quantum yields of DBK and TBK is also consistent with the presence of singlet state α -cleavage in both ketones. The introduction of a methyl group in the ortho position of the phenyl ring in TBK introduces a second singlet state ketone reaction, δ -hydrogen-atom abstraction. This reaction is faster than α -cleavage in the S_1 state, but proceeds with a low quantum efficiency. A δ -hydrogen-atom-induced internal conversion is proposed to be a major mechanism for the deactivation of the S_1 state of TBK. This deactivation of S_1 serves to reduce the efficiency of intersystem crossing and competes effectively with α -cleavage in S_1 . For TBK, *o,o'*-dimethyl TBK and mesitylmethyl benzyl ketone, which all show fast singlet state hydrogen-atom abstraction, the quantum yields of fluorescence and α -cleavage decrease. On the basis of the assumption of a certain (20%) participation of singlet state α -cleavage and fast δ -hydrogen-atom abstraction, a general mechanism and rate constants of each process were estimated for DBK and TBK.

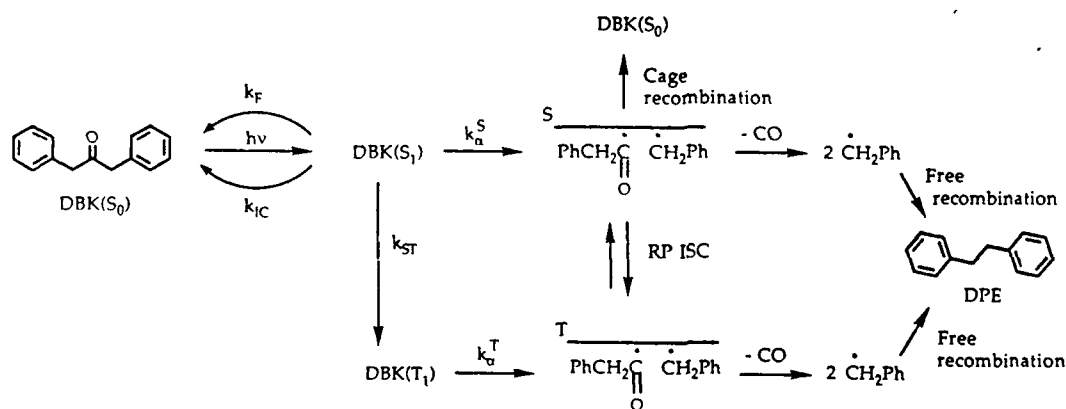
1. Introduction

Dialkyl ketones and α -aryl-substituted dialkyl ketones undergo two dominant unimolecular primary photochemical reactions: α -cleavage to produce a geminate radical pair (RP) and (if the structure allows) intramolecular hydrogen-atom abstraction to produce a biradical [1]. Intramolecular hydrogen-atom abstraction reactions of dialkyl ketones, the best studied of which is the primary photochemical process of γ -hydrogen-atom abstraction, are known to occur in both the singlet and triplet states [1]. Although the cases examined are few in number, the γ -hydrogen-atom abstraction in the singlet state may occur with a faster rate than in the triplet [1b, 2]. For example, the rate of γ -hydrogen-atom abstraction for singlet 2-pentanone is $1.8 \times 10^8 \text{ s}^{-1}$, whereas the rate of γ -hydrogen-atom abstraction for triplet 2-pentanone is only $0.13 \times 10^8 \text{ s}^{-1}$, so that the singlet is over an order of magnitude more reactive than the triplet [2]. In contrast, the primary photochemical process of α -cleavage generally occurs

much faster in the triplet than in the singlet state [1, 3]. For example, triplet di-*tert*-butyl ketone undergoes α -cleavage with a rate of $8 \times 10^9 \text{ s}^{-1}$, whereas the singlet cleaves with a rate of $6 \times 10^7 \text{ s}^{-1}$, so that in this case the triplet is over two orders of magnitude more reactive than the singlet [3]. The α -cleavage reaction has been proposed to exhibit different correlation diagrams for the singlet and triplet states of simple dialkyl ketones, with the singlet correlating with an excited state of the singlet RP product and the triplet correlating, through a surface crossing with a higher energy triplet of the ketone, with the ground state of the triplet RP product [4].

For over 20 years the photochemistry of dibenzyl ketone (DBK, 1, Scheme 1) and its derivatives has been treated as a paradigm for dialkyl ketones undergoing α -cleavage at room temperature in inert non-viscous solvents. This paradigm has taught that the S_1 state of DBK undergoes nearly quantitative intersystem crossing (ISC) to the T_1 state, which undergoes efficient α -cleavage to generate a primary geminate triplet phenacyl–benzyl RP. The phenacyl radicals decarbonylate and the observed products are formed by recombination

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Scheme 1.

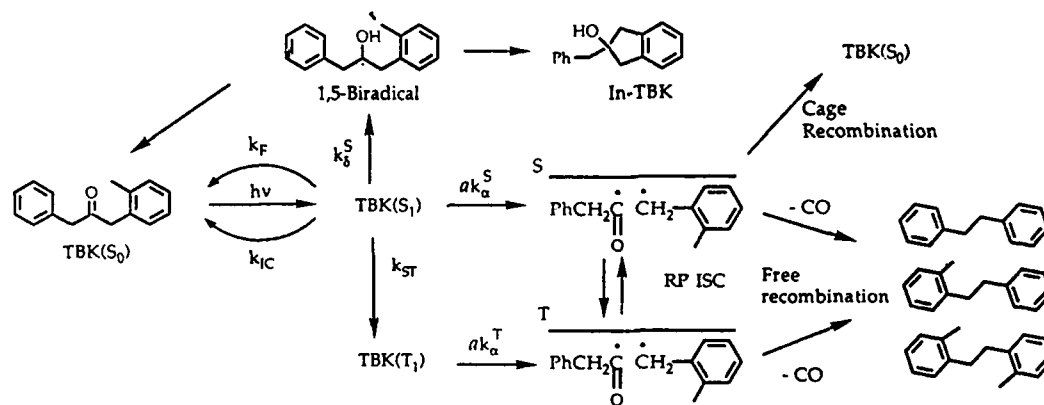
of free benzyl radicals (Scheme 1). The qualitative basis of this paradigm is firmly established from experiments involving specific triplet quenching [5], chemically induced dynamic nuclear polarization (CIDNP) spectra [6], chemically induced dynamic electron polarization (CIDEP) spectra [7], magnetic isotope effects [8] and magnetic field effects [9]. Although such experiments are generally not sufficiently quantitative to define the exact percentage of α -cleavage of the T_1 state relative to S_1 , it has been accepted that the contribution of S_1 to products from α -cleavage must be minor.

However, the paradigm of nearly exclusive α -cleavage of DBK from the T_1 state has been challenged by two recent reports. The first involves the direct measurement of the appearance of the benzyl radical, one of the α -cleavage products, by picosecond transient spectroscopy [10], and the second involves the measurements of the coefficient of polarization in a CIDNP experiment and its comparison with theoretical calculations based on the contribution of both singlet and triplet precursors to α -cleavage [11]. In the former [10], the rate of appearance of benzyl radicals after picosecond laser excitation of DBK was found to be equal to the rate of disappearance of the transient ascribed to the S_1 state of DBK. This observation is consistent with the singlet state decay being the rate-limiting stage for α -cleavage and does not require the involvement of the triplet state in the formation of the benzyl radical. From the principle of mechanistic economy, we can therefore associate the α -cleavage product as arising exclusively from an S_1 primary photochemical process, *i.e.* $S_1 \rightarrow {}^1\text{RP} \rightarrow \text{benzyl radicals}$ (Scheme 1). However, the result is also consistent with the rate-limiting ISC from S_1 to T_1 followed by fast α -cleavage, $S_1 \rightarrow T_1 \rightarrow {}^3\text{RP} \rightarrow \text{benzyl radicals}$ (Scheme 1). In the CIDNP experiments [11], based

on the measurements of nuclear polarization enhancement factors as a function of temperature and the quantum yields of DBK decomposition, it was computed that the photolysis of DBK in chloroform results in 75% α -cleavage of DBK from S_1 and 25% from T_1 . In toluene, the estimated contribution of the singlet drops to 25%. However, these CIDNP results refer only to the small fraction of primary RPs which undergo cage recombination together with the recombination of free, uncorrelated RPs. Since the cage effect for DBK in homogeneous solution should be very small (close to zero), based on the measurements for relevant ketones [12], and free RP recombination goes through three-quarters of triplet and one-quarter of singlet RPs, the results of the CIDNP experiments are not directly proportional to the fraction of α -cleavage that occurs in the singlet relative to the triplet excited state of DBK molecules.

Neither of the above results, *per se*, presents a serious indictment of the validity of the conventional paradigm of the photochemistry of DBK proceeding dominantly from the T_1 state. However, the importance of the mechanism of photolysis of DBK and its derivatives to the field of magnetic effects on photoreactions, and the critical role of the triplet state and the triplet RP in producing these effects and in quantitative simulations of magnetic effects, provided a powerful incentive to seek a more definitive and quantitative evaluation of the extent of participation of the S_1 and T_1 states in the primary process of α -cleavage of this ketone.

By sensitization with triplet acetone and by reaction quenching with isoprene [13], we have shown that intramolecular δ -hydrogen-atom abstraction in *o*-tolylmethyl benzyl ketone (TBK, 2) proceeds exclusively in the singlet excited state (Scheme 2). This observation, together with the



Scheme 2.

absence of a magnetic field effect on the yield of 2-benzyl-2-indanole, the product of intramolecular δ -hydrogen-atom abstraction on photolysis of TBK in different micelles, and the occurrence of a strong magnetic field effect on the yield of the diphenylethane coupling products [14], suggests the possible participation of the singlet excited state in the photochemistry of DBK and its derivatives.

To test for the possibility of singlet state photochemistry for DBK and its derivatives, we selected the following strategies. First, is the comparison of the quantum yields of photolysis and the fluorescence of ketones based on a general reaction scheme. Measurements of the quantum yields of photolysis and fluorescence of DBK and TBK and CIDNP measurements of the relative rate constants of α -cleavage allow an estimation to be made of the absolute rate constants of α -cleavage in the singlet state and the fraction of the singlet state α -cleavage. The second more quantitative approach is to determine the relative yield of products formed from the photolysis of DBK and TBK resulting from triplet α -cleavage and singlet α -cleavage (ϕ_r^{OT}/ϕ_r^{OS}) by quenching experiments. The data obtained from these quenching experiments can then be fitted to a master Stern-Volmer equation which quantitatively relates the fraction of S_1 and T_1 reactions to the quenching data [15]. The value of ϕ_r^{OT}/ϕ_r^{OS} can be used as an adjustable parameter to fit the data to the master equation. This analysis can then be extended to TBK which is also capable of undergoing δ -hydrogen-atom abstraction in the singlet state.

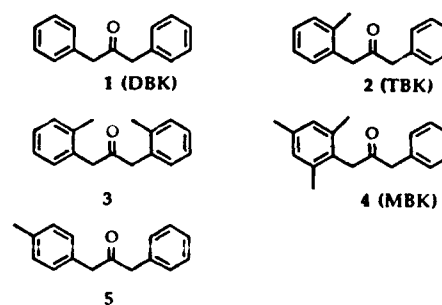
The results of our findings are that, although the dominant pathway for α -cleavage of DBK is indeed from the triplet state, a non-negligible fraction of α -cleavage (approximately 20%–30%) occurs from the singlet state. In addition, δ -hydrogen-atom abstraction is a competitive reaction

from the singlet state, but not the triplet state, for derivatives of DBK possessing an *o*-methyl substituent. The latter reaction which proceeds with low quantum efficiency is found to induce an additional mechanism for the internal conversion of the S_1 state of *o*-methyl derivatives of DBK.

2. Experimental details

2.1. Materials

DBK (**1**) was obtained from Aldrich and was purified by recrystallization from ethanol. Ketones **2–5** (Scheme 3) were prepared and purified following literature methods [16]. 1,3-Cyclohexadiene (CHD) and isoprene were obtained from Aldrich and were distilled twice under argon before use. Benzene, cyclohexane and acetone (Spectrometric grade) were obtained from Aldrich and were used as received after checking the emission of the solvent. Benzene as a solvent for fluorescence quenching experiments was purified by washing with sulfuric acid and drying over P_2O_5 followed by distillation.



Scheme 3.

2.2. Measurements of spectroscopic properties

The UV spectra of the ketones were recorded on a Perkin-Elmer Lambda Array 3840 spectrometer, and the fluorescence spectra were recorded on a Perkin-Elmer LS-50 spectrofluorometer. The fluorescence quantum yields were measured in cyclohexane without degassing of the solutions. The emission spectra of acetone (optical density, about 0.1) on 295 nm excitation were compared with optically equivalent solutions of the ketones.

2.3. Quantum yield measurements

Argon-bubbled solutions of the ketones (0.10 M) were irradiated on a merry-go-round apparatus in Pyrex tubes in an Ar atmosphere through 0.002 M K_2CrO_4 in 1% aqueous K_2CO_3 (maximum transmission, 313 nm) [17] with a 450 W Hanovia medium pressure mercury lamp at room temperature. Gas chromatographic (GC) analyses of the photolysis products were carried out with an internal standard (usually hexadecane or diphenylmethane) on a Hewlett Packard 5890 gas chromatograph with a 25 m Carbowax 20M or an SE-30 capillary column. Relative quantum yields were measured with simultaneous irradiation of DBK. For the absolute measurement of the quantum yield of DBK, 0.25 M valerophenone in *tert*-butanol was used as an actinometer [18]. The quantum yield of valerophenone disappearance was taken as 1.0 [18]. Conversions of ketones were kept under 20%.

To determine the relative quantum yields of the α -cleavage reaction of TBK and 5, the possible error due to potentially different optical density changes was minimized by irradiating benzene solutions containing both DBK and one of these two ketones. The conversions were kept to low values (1.5%–3%). The quantum yield of TBK in this method (0.29) was quite similar to that measured with a merry-go-round apparatus (0.31).

2.4. Quenching experiments

For quenching experiments, aerated solutions were used after confirming that argon purging did not affect the quantum yield of photolysis of DBK. The concentrations of ketones in benzene were about 0.025 M in reaction quenching experiments with CHD or isoprene. In the case of CHD quenching, the results were corrected for the UV absorption of CHD at the excitation wavelength (313 nm). The fluorescence quenching of DBK and TBK with isoprene and CHD was measured in benzene by excitation at 320 nm while monitoring the intensity of emission at 410 nm. The maximum

quencher concentrations was 5 M and the quenching data were corrected for absorption changes at the excitation wavelength.

2.5. CIDNP spectra

The CIDNP experiments were carried out on a Bruker WM-250 nuclear magnetic resonance (NMR) spectrometer. Photoexcitation was provided by an Oriel 1 kW high pressure Xe–Hg lamp through a water filter and optical pipe with mirrors perpendicular to the sample. The ketones in acetonitrile- d_3 (about 9×10^{-3} M) were degassed by argon bubbling. The relative intensities of the polarized methylene signals in TBK and MBK used for calculations were measured by computer subtraction of the "light" and "dark" spectra of the ketones. Spin-lattice relaxation times were measured by the inversion-recovery method with the same NMR spectrometer.

3. Results

3.1. Product analysis

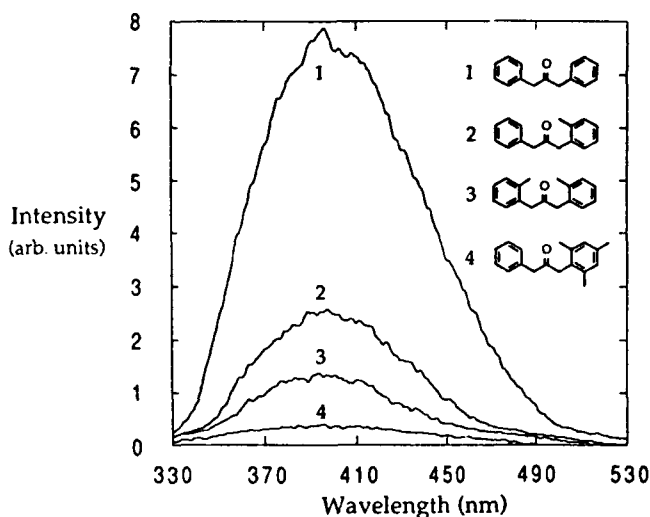
The structures of the products (diphenylethanes and indanoles) produced by the photolysis (313 nm) of DBK (1) and TBK (2) at room temperature in benzene are shown in Schemes 1 and 2. Details of the structural analysis are reported elsewhere [13, 14]. The photochemical products from *o,o'*-dimethyl DBK (3) and mesitylmethyl benzyl ketone (MBK, 4) are similar (with appropriate substituents) to those to TBK. The mass balances are very good (approximately 90%) for each system. In the case of DBK, 1,2-diphenylethane (DPE) was found to be the only product detectable by GC analysis and is formed in quantitative yield ($98\% \pm 3\%$). For the photolysis of TBK and MBK, DPEs (1:2:1 statistical mixture of the three possible benzyl radical coupling products) are produced in addition to the indanole expected from the cyclization of the 1,5-biradical produced from δ -hydrogen-atom abstraction. Although the yield of indanole is low for TBK (6%), it is substantial for MBK (39%).

3.2. Optical spectroscopy of DBK and some derivatives

The absorption spectra of ketones 1–4, *p*-methyl DBK (5) and acetone in cyclohexane at room temperature were recorded. The maximum absorption wavelengths and the extinction coefficients at the maxima are collected in Table 1. The fluorescence spectra (295 nm excitation) of the ketones were determined in aerated cyclohexane

TABLE 1. UV data of ketones in cyclohexane

Ketone	λ_{\max} (ϵ , n, π^*)	λ_{\max} (ϵ , π, π^*)	$\epsilon(313)$
1	295 (240)	266 (350), 260 (410)	150
2	295 (250)	265 (480), 261 (480)	150
3	297 (280)	265 (720)	130
4	296 (270)	267 (480), 261 (470)	140
5	295 (285)	267 (530), 261 (512)	180
Acetone	280 (24)		5

Fig. 1. Emission spectra of DBK (1), TBK (2), *o,o'*-dimethyl DBK (3) and MBK (4) in cyclohexane ($\lambda_{\text{ex}}=295$ nm).TABLE 2. Relative quantum yields of formation of DPEs (α -cleavage) and indanoles, relative fluorescence quantum yields and preferential α -cleavages obtained from CIDNP results of dibenzyl ketone derivatives

Ketone	DPE ^a	Indanole ^a	Fluorescence ^b	CIDNP ^c
1	1.00 ^d	0	1.00	1.0
2	0.35 ^e	0.023	0.30	2.1
3	0.26	0.032	0.16	—
4	0.13	0.083	0.05	2.5
5	1.08 ^e	—	1.06	1.5 ^f

^aError is determined to be $\pm 10\%$.^bError is determined to be $\pm 6\%$. Excitation wavelength, 295 nm.^cRatio of α -cleavage compared with the signal of the benzyl group.^dQuantum yield of 1 is estimated to be 0.84 ± 0.06 .^eEstimated from a mixed solution with 1.^fTaken from ref. 19.

solution at room temperature. Representative fluorescence spectra (DBK, TBK, 3, MBK) are shown in Fig. 1 and the relative quantum yields of fluorescence are collected in Table 2. The maximum emission wavelengths from these ketones are in the range 394–400 nm and no trend in

emission wavelength shift is observed. The absolute fluorescence quantum yield of DBK in cyclohexane was determined to be 0.006 compared with that of acetone ($\Phi_F = 9.3 \times 10^{-4}$) [20].

3.3. Quantum yields

The relative quantum yields of appearance of the products were measured by irradiating equal-volume degassed samples in a merry-go-round apparatus or by photolysis of mixed solutions of two ketones (concentrations precisely known, about 1:1 in the ketones). These results are summarized, together with the relative fluorescence yields, in Table 2. The absolute quantum yields (excitation at 313 nm) of disappearance of DBK and of appearance of DPE were determined with reference to the disappearance of valerophenone in *tert*-butanol as an actinometer [18]. The value determined (0.84 ± 0.06) is in reasonable agreement with the literature [5, 21]. As a control, the absorption of the photolyzed solutions of DBK as a function of partial conversion was monitored and no reduction of the optical density of the sample at the excitation wavelength (313 nm) was observed. This phenomenon has been noted previously [5b] and is suggestive of the production of a light-absorbing species possessing a large extinction coefficient relative to DBK at 313 nm. Thus the quantum yield of 0.84 is a lower limit.

3.4. CIDNP studies

The proton NMR spectra of TBK and MBK in acetonitrile- d_3 , during and before irradiation, were recorded. During the irradiation of TBK, the methylene proton signals of the starting ketones (3.73, 3.70 ppm) appear in the emission. At the same time, the methylene proton signals of the three escape products of decarbonylation (DPEs) are observed as enhanced absorption. The spin-lattice relaxation times (T_1) of the methylene protons of the benzyl group (3.70 ppm) and of the *o*-tolyl-methylene protons (3.73 ppm) are 4.66 and 4.09 s respectively in argon-bubbled acetonitrile- d_3 solution. The CIDNP spectra do not contain any signal associated with the products of intramolecular hydrogen-atom abstraction.

3.5. Quenching by isoprene and CHD

Stern–Volmer quenching of the fluorescence and the disappearance of the starting material in the photolysis of DBK were determined by employing isoprene and CHD as quenchers. Results for the quenching of DBK and TBK with isoprene are shown in Figs. 2 and 3 respectively. For TBK the results for isoprene quenching of the appearance

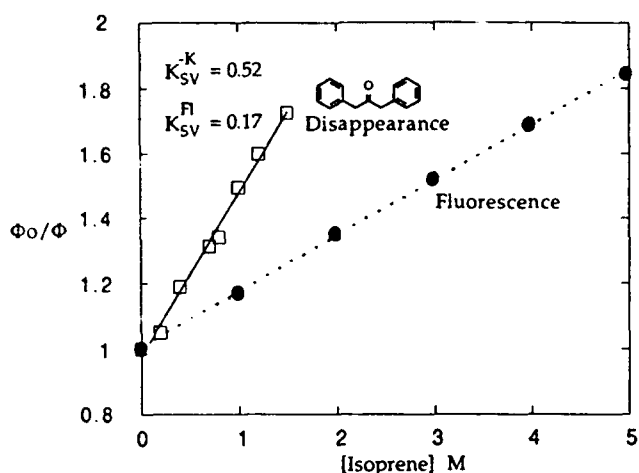


Fig. 2. Stern-Volmer plots of isoprene quenching of DBK photolysis (open squares) and fluorescence (filled circles).

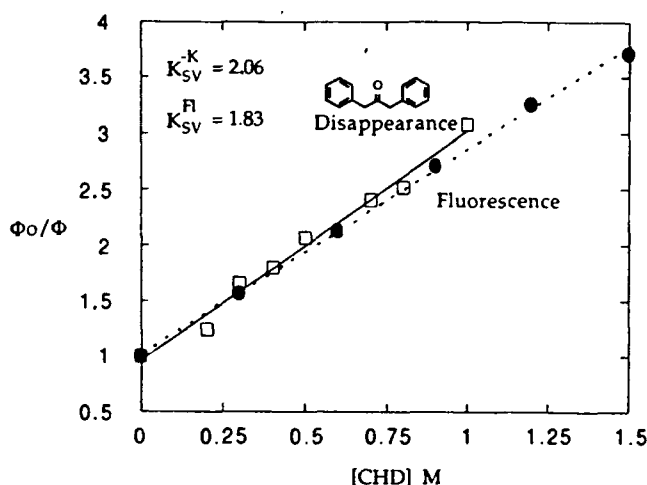


Fig. 4. Stern-Volmer plots of CHD quenching of DBK photolysis (squares) and fluorescence (filled circles).

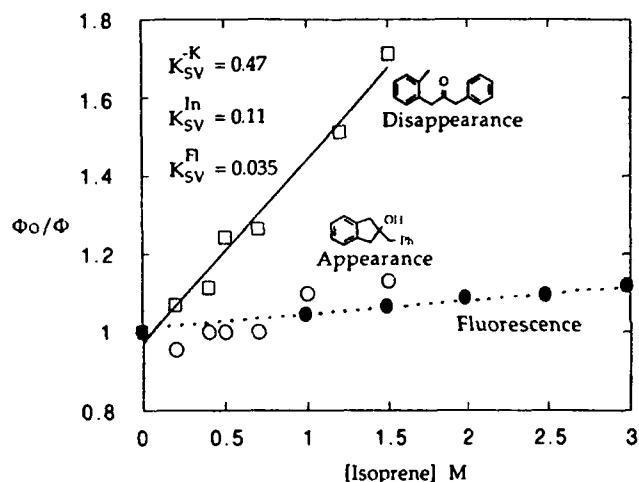


Fig. 3. Stern-Volmer plots of isoprene quenching of TBK fluorescence (filled circles) and photolysis (squares represent the disappearance of starting ketone and open circles represent the formation of indanole).

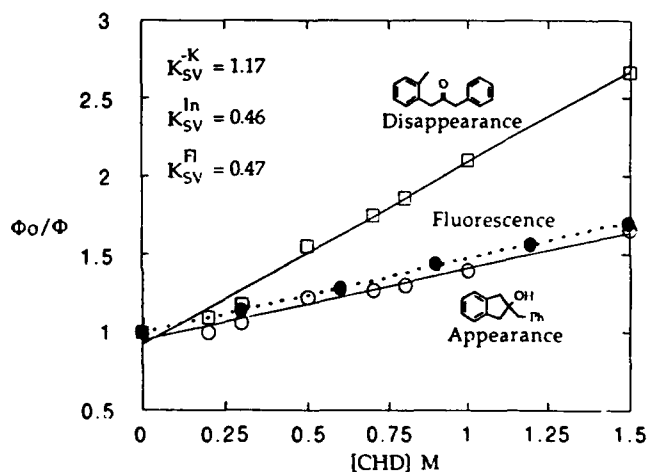


Fig. 5. Stern-Volmer plots of CHD quenching of TBK fluorescence (filled circles) and photolysis (disappearance of TBK (squares) and formation of indanole (open circles)).

of the indanole product are also shown in Fig. 3. Analogous results for the quenching of DBK and TBK by CHD are shown in Figs. 4 and 5 respectively. From the linear portions of the quenching plots, the slopes of the Stern-Volmer plots of fluorescence and reaction were determined and are summarized as Stern-Volmer constants in Table 3, together with the literature results [5a].

4. Discussion

4.1. Reaction scheme

The working paradigm for the photolysis of DBK, based on substantial experimental evidence, is summarized in Scheme 1. The unimolecular processes available for the deactivation (rate con-

TABLE 3. Stern-Volmer slopes from quenching studies of DBK (1) and TBK (2) with dienes in benzene^a

Quenching	1 (M ⁻¹) ^b	2 (M ⁻¹) ^b
CHD, fluorescence ^c	1.83 ± 0.03	0.47 ± 0.01
Isoprene, fluorescence ^c	0.17 ± 0.02	0.035 ± 0.001
Pentadiene, fluorescence ^d	0.21	—
CHD, disappearance of ketone ^c	2.06 ± 0.10	1.17 ± 0.05
CHD, indanole formation ^c	—	0.46 ± 0.03
Isoprene, disappearance of ketone	0.52 ± 0.02	0.47 ± 0.03
Isoprene, indanole formation	—	0.11 ± 0.03
Pentadiene, disappearance of ketone ^d	0.91	—

^aExcitation at 320 nm, emission at 400 or 410 nm.

^bStern-Volmer slope.

^cCorrected by the UV absorption of mixture at 320 nm.

^dTaken from ref. 5.

stants) of the S_1 state are fluorescence (k_F), internal conversion (k_{IC}), intersystem crossing to T_1 (k_{ST}) and α -cleavage (k_α^S), and the processes available to T_1 are intersystem crossing to S_0 , phosphorescence and α -cleavage (k_α^T). In the case of the *o*-tolyl derivatives of DBK, we include the possibility of δ -hydrogen-atom abstraction in both the S_1 state (k_δ^S) and the T_1 state (k_δ^T) [13].

The efficiency of the fluorescence from DBK and its derivatives is of the order of a few per cent, at best, so that k_F is negligible compared with the rate constants causing deactivation of S_1 , and the fluorescence step can be ignored in terms of its contribution to the lifetime of S_1 and to the quantum efficiencies of reaction in all cases. Although the internal conversion step is usually ignored for ketones, we consider it explicitly since we suspect a specific "chemically promoted" internal conversion may result for DBK or TBK [13, 22]. From these considerations the rate constant of total deactivation (k_S) of the singlet state of DBK is given, in a good approximation, as the sum of $k_\alpha^S + k_{ST} + k_{IC}$. In the case of TBK, which can undergo δ -hydrogen-atom abstraction, we must include the appropriate rate constant (k_δ^S) for deactivation of the excited singlet state.

In the case of the triplet state of DBK, the rate of α -cleavage calculated from our DBK reaction quenching data by isoprene is $1.0 \times 10^{10} \text{ s}^{-1}$, which agrees with previous measurements [5a], and is far greater than the rate of phosphorescence or ISC to S_0 or any known photophysical deactivation from "model" ketone triplet states. Thus the rate constant for total deactivation of the triplet (k_T) of DBK can be given, in an excellent approximation, by the value of k_α^T . Furthermore, the quantum yield of DPE formation from the triplet ketone should be a good approximation to the quantum yield of ISC, Φ_{ST} . We ignore the contribution of the triplet- δ -hydrogen-atom abstraction because of recent evidence that this reaction cannot compete with α -cleavage of TBK (based on quenching and sensitization experiments) [13].

The fluorescence quantum yield of DBK ($\Phi_F = 0.006$) is determined to be six times larger than that of acetone. The fluorescence efficiency of TBK ($\Phi_F = 0.0018$) is smaller than that for DBK. The smaller value of Φ_F for TBK is attributed to the occurrence of a competing fast hydrogen-atom abstraction reaction from the excited singlet state. The relative fluorescence quantum yield of TBK indicates that the singlet lifetime of TBK is more than three times smaller than that of DBK, since the long-wavelength absorptions of DBK and TBK are nearly identical (Table 1). The Φ_F ratio for

TBK and DBK is in good agreement with the ratio of the CHD fluorescence quenching efficiencies of TBK and DBK (0.26). No reduction in the absorption at 313 nm was reported by Robbins and Eastman [5b] during the irradiation of DBK in benzene at that wavelength. To reduce the experimental error due to the potentially different optical density changes, the relative quantum yield of α -cleavage from DBK and TBK was measured from the irradiation of mixed samples. Employing this procedure and eqn. (1) (see Section 4.2), the measured relative (*vs.* DBK) quantum yield of α -cleavage of TBK is 0.35, which gives an absolute value of 0.29.

4.2. Estimation of the singlet α -cleavage contribution based on a general reaction scheme

The first approach to estimate the singlet α -cleavage contribution is the comparison of the quantum yields of photolysis and fluorescence of the ketones (eqns. (1)–(4)) based on the general reaction schemes for DBK and TBK (Schemes 1 and 2)

$$\Phi_F(\text{DBK}) = \frac{k_F}{k_F + k_\alpha^S + k_{IC} + k_{ST}} \quad (1)$$

$$\Phi_\alpha(\text{DBK}) = \frac{k_\alpha^S + k_{ST}}{k_F + k_\alpha^S + k_{IC} + k_{ST}} \quad (2)$$

$$\Phi_F(\text{TBK}) = \frac{k_F}{k_F + a k_\alpha^S + k_{IC} + k_{ST} + k_\delta^S} \quad (3)$$

$$\Phi_\alpha(\text{TBK}) = \frac{a k_\alpha^S + k_{ST}}{k_F + a k_\alpha^S + k_{IC} + k_{ST} + k_\delta^S} \quad (4)$$

In eqn. (1)–(4), k_F , k_α^S , k_{IC} , k_{ST} and k_δ^S are the rate constants of fluorescence, singlet α -cleavage, singlet non-radiative decay, ISC and singlet δ -hydrogen-atom abstraction; a is the ratio of the α -cleavage rates of TBK and DBK.

The rate of benzyl radical formation in the photolysis of DBK has already been measured directly by transient spectroscopy to be $4.6 \times 10^8 \text{ s}^{-1}$ [10]. Since the shape and extinction coefficients of the absorption spectra of DBK and TBK are quite similar (Table 1), the rate of fluorescence of these two ketones should be almost the same [22, 23]. We also assume that the rates of ISC and internal conversion of DBK and TBK are similar due to their similar structures [19, 23].

For calculation according to eqns. (1)–(4) we need to know a , the ratio of the rates of α -cleavage of the benzyl-carbonyl and *o*-methylbenzyl-carbonyl bonds in the S_1 state. The relative in-

tensities of the polarized signals of the corresponding protons in a CIDNP spectrum of the molecule may be employed to obtain this information [24]. In the CIDNP spectrum of TBK the intensities of the emissive signals of the methylene protons of the starting ketone (3.73, 3.70 ppm) are different. The spin-lattice relaxation time of the methylene protons in the benzyl group is 1.15 times larger than that of the methylene protons in the *o*-methylbenzyl group in TBK. Since the magnetic parameters of the RPs formed during α -cleavage of both bonds next to the carbonyl are almost the same and the intensity of the polarized signal divided by the relaxation time is proportional to the concentration of the RPs formed, the polarized signal intensities are proportional to the rate of α -cleavage of the bonds [24]. The polarized signal of the *o*-methylbenzyl group (the difference between the signal on photolysis and in the dark) is 1.8 times larger than that of the benzyl group; therefore, since the spin-lattice relaxation time of these protons is 1.15 times smaller than that of those in the benzyl group, the cleavage of the *o*-methylbenzyl bond is 2.1 times faster than that of the unsubstituted benzyl bond. From these data the α -cleavage reactivity of TBK is estimated to be 1.55 times $((2.1 + 1)/2)$ larger than that of DBK. By a similar analysis of CIDNP and relaxation time data, cleavage of the *o,o,p*-trimethylbenzyl bond in MBK is found to be 2.5 times as efficient. The increase in the rates of α -cleavage in the triplet state of α -phenyl alkyl ketones with the addition of electron-donor substituents at the aromatic ring [24] is probably determined by the larger thermodynamic stability of the product radicals [25]. The increase of 2.5 in the rate of α -cleavage of MBK is quite similar to the inductive effect of methyl groups on the rate of α -cleavage [26].

Since the CIDNP spectra correspond to a triplet multiplicity of the excited state precursor [6], the experimental ratio of the α -cleavage rates of the two bonds is measured for the molecule in the excited triplet state. The ratio a of the singlet α -cleavage rates of the benzyl and *o*-methylbenzyl bonds is assumed to be the same as in the triplet states.

Since ISC is the rate-determining process in the triplet state α -cleavage in both DBK and TBK, the contribution of singlet state cleavage to the total α -cleavage of the ketones is determined by the ratio $k_a^S/(k_{ST} + k_a^S)$. From the experimental data on the quantum yields of fluorescence and α -cleavage, and based on the rates determined from eqns. (1)–(4) approximately 25% and 35%

of the α -cleavage reaction of DBK and TBK respectively occurs from the singlet state.

Since this method of calculation contains a few assumptions and the error of each experimental method used is at least 10%, the exact contribution of singlet α -cleavage cannot be quantitatively determined in this way. However, the presence of certain contributions of singlet α -cleavage in DBK and TBK is consistent with the results. An attempt to use a more quantitative method of estimating this singlet contribution is presented in the following section.

4.3. Estimation of the singlet α -cleavage contribution by fitting the quenching data to a master Stern–Volmer equation

If α -cleavage to produce DPE occurs from both the singlet and triplet states of DBK, the data in Figs. 2 and 4 should not be strictly linear. However, an analytical expression or master equation [15] (eqn. (5)) for the Stern–Volmer plot of both the singlet and triplet state products reveals that close approximation to a straight line will result experimentally when the values of the Stern–Volmer constants ($k_q\tau$) for the reactions in each state are comparable in value. In eqn. (5)

$$\frac{\Phi_r^0}{\Phi_r} = \{1 + k_q^S \tau_S^0 [Q]\} \{1 + k_q^T \tau_T^0 [Q]\} \left\{ \frac{1 + (\phi_r^{ST}/\phi_r^{OS})}{1 + (\phi_r^{ST}/\phi_r^{OS}) + k_q^T \tau_T^0 [Q]} \right\} \quad (5)$$

τ_S^0 , τ_T^0 and ϕ_r^{ST}/ϕ_r^{OS} are the singlet and triplet lifetimes in the absence of quencher and the ratio of the triplet and singlet α -cleavage quantum yields in the absence of quencher respectively. The terms $k_q^S \tau_S^0$ and $k_q^T \tau_T^0$ are the Stern–Volmer constants for quenching of product formation from the singlet and triplet states respectively. The quantity $[Q]$ is the quencher concentration, an experimental variable; the quantity Φ_r^0/Φ_r is the ratio of the disappearance of the ketone in the absence and presence of the quencher, and is an experimental observable. In eqn. (5), we have three unknown quantities, ϕ_r^{ST}/ϕ_r^{OS} , $k_q^S \tau_S^0$ and $k_q^T \tau_T^0$, and we are able to measure Φ_r^0/Φ_r as a function of $[Q]$. We make no assumptions concerning the other chemical pathways occurring from S_1 . The singlet Stern–Volmer parameter ($k_q^S \tau_S^0$) is independent of the type of singlet state process monitored experimentally. Therefore the value of $k_q^S \tau_S^0$ can be obtained from an independent experiment measuring the quenching of the fluorescence of DBK, and by identifying the experimental value of the Stern–Volmer constant for fluorescence ($k_q^F \tau_S^0$)

with the desired value for quenching of the singlet state, *i.e.* $k_q^F \tau_S^0 = k_q^S \tau_S^0$. We are then left with two unknowns ($k_q^T \tau_T^0$ and ϕ_r^{OT}/ϕ_r^{OS}) in eqn. (5). Although we cannot determine $k_q^T \tau_T^0$ directly, we can approximate $k_q^T \tau_T^0$ from the experimental quenching curves and then use ϕ_r^{OT}/ϕ_r^{OS} as an adjustable parameter to achieve the best fit to eqn. (5).

As can be seen from Figs. 2–5, there is a significant difference between the slopes of fluorescence quenching and ketone disappearance for DBK and TBK with isoprene as quencher and for TBK with CHD as quencher. However, for DBK with CHD as quencher, the curves for the fluorescence quenching and for the disappearance of DBK virtually overlap. For this system most of the quenching occurs in the singlet state, because the singlet lifetime of DBK is relatively long [13] and the singlet quenching rate constant of CHD is large [27]. Although there is slightly higher quenching for the disappearance of DBK than for fluorescence, the difference is too small to use eqn. (5) to estimate the extent of singlet α -cleavage.

We can estimate the value of $k_q^T \tau_T^0$ by subtraction of the slope for the fluorescence quenching from the slope for the quenching of the disappearance of ketone. From the data in Fig. 2 (DBK–isoprene), the slope for the quenching of DBK disappearance is 0.52 M^{-1} and the approximate value of $k_q^F \tau_S^0$ derived from the slope for the quenching of DBK fluorescence is 0.17 M^{-1} (Table 3). The approximate value of $k_q^T \tau_T^0$ is given by the difference between the quenching slope, $k_q^T \tau_T^0$ and $k_q^F \tau_S^0$, *i.e.* 0.35 M^{-1} . By inserting the values of $k_q^T \tau_T^0 = 0.35 \text{ M}^{-1}$ and $k_q^S \tau_S^0 = 0.17 \text{ M}^{-1}$ into eqn. (5) and employing the value of ϕ_r^{OT}/ϕ_r^{OS} as an adjustable parameter in a data base program, the family of curves (1%–100% singlet) shown in Fig. 6 is generated. Some representatives of the percentage singlet yields are shown to the right of the displayed curves and the experimental data are shown as filled circles. Visual inspection of Fig. 6 reveals that the “best fit” for the singlet contribution to the α -cleavage reaction is in the range 15%–25%.

Following a similar procedure for the fitting of the quenching of the photolysis of TBK with isoprene and CHD, the curves shown in Figs. 7 and 8 were generated. In these curves the approximate values of $k_q^T \tau_T^0$ employed were 0.43 M^{-1} and 0.70 M^{-1} for isoprene and CHD respectively. The “best fits” are in the range 5%–25% for the singlet reaction for isoprene as quencher and 20%–30% for the singlet reaction with CHD as quencher. When the unadjusted slopes of the

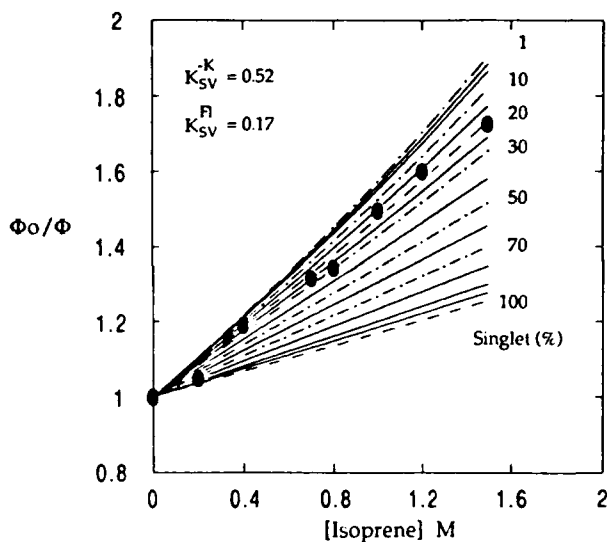


Fig. 6. A comparison of the experimental quenching results of DBK photolysis by isoprene (filled circles) with the numerical simulation ($k_q \tau_T = 0.35$) of the quenching plots on variation of the singlet contribution to the reaction (eqn. (5)).

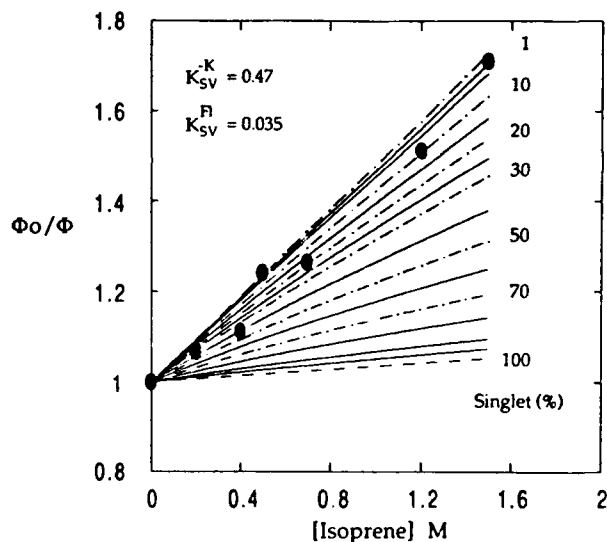


Fig. 7. A comparison of the experimental quenching of TBK photolysis by isoprene (filled circles) with the numerical simulation ($k_q \tau_T = 0.43$) on variation of the singlet contribution to the reaction (eqn. (5)).

quenching of the disappearance of ketone were used as $k_q^T \tau_T^0$, 30%–50%, 15%–25% and 35%–55% singlet contributions were estimated in DBK–isoprene, TBK–isoprene and TBK–CHD.

4.4. Quantum yields for the primary processes of DBK

Let us consider the possibility that the S_1 state undergoes α -cleavage but that the primary singlet geminate radical pair, ^1RP in Scheme 1, which is produced recombines without the formation of

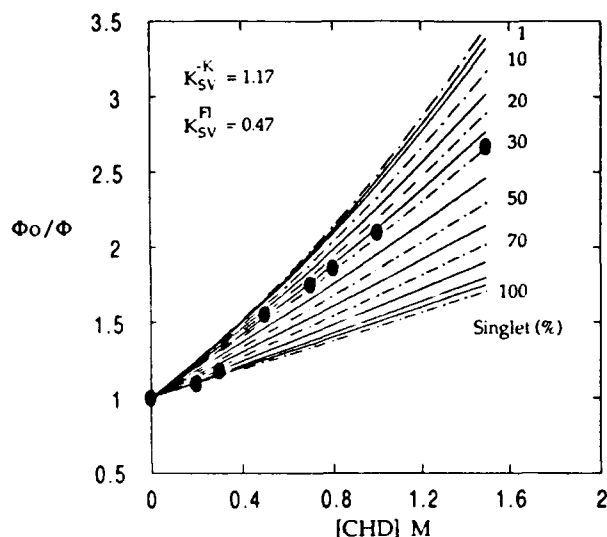


Fig. 8. A comparison of the experimental quenching of ^1DBK photolysis by CHD (filled circles) with the numerical simulation ($k_q\tau_T = 0.7$) on variation of the singlet contribution to the reaction (eqn. (5)).

products, *i.e.* there is a large cage effect for ^1RP . Since the absolute quantum yield for product formation is slightly less than unity, the reaction inefficiency could be attributed to such a process. Our analysis is concerned with S_1 states which lead to the measurable formation of product, so that we will consider reversible α -cleavage from the S_1 state together with internal conversion and associate the process with the other photophysical processes returning S_1 to the ground state. However, we can reject the possibility of a significant cage effect in S_1 to the ground state. However, we can reject the possibility of a significant cage effect in S_1 based on the following argument. On the assumption that 20% of the total DPE product results from the α -cleavage of S_1 , from the measured total quantum yield for DPE formation (0.84), the maximum quantum yield for α -cleavage from S_1 is approximately 0.16 and the quantum yield from T_1 is approximately 0.58. If the reaction inefficiency of 0.16 is due to cage recombination of a primary singlet geminate pair, then the cage effect will be about $0.16/(0.16+0.16)$ or around 50%. We reject this value as unrealistically high from the observation that the photolysis of stereoisomerically pure α,α' -dimethyl dibenzyl ketone (either meso or D,L) in benzene does not lead to more than 1% stereoisomerization, so that the cage effect of the RP from this ketone cannot be more than 1% [12a]. We conclude that the RP from α,α' -dimethyl dibenzyl ketone should be similar to that from DBK, so that an efficient cage recombination following α -cleavage in S_1 of DBK

is not the dominant cause of the reaction inefficiency.

The total quantum yield of reaction (formation of DPE) Φ_{DPE} is the sum of the reaction from S_1 (Φ_{DPE}^S) and T_1 (Φ_{DPE}^T). The experimental value of Φ_{DPE} is 0.84 so that there is a reaction inefficiency at some point. Since we have concluded that T_1 produces products (DPE) with essentially unit efficiency and that S_1 does not undergo significant cage effect, the source of inefficiency must occur in S_1 due to a radiationless deactivation with $\Phi_D^S = 0.16$. The sum of $\Phi_{\text{DPE}}^S + \Phi_{\text{DPE}}^T + \Phi_D^S = 1.00$, so that the yield of ISC is equal to the yield of DPE from the triplet reaction, *i.e.* $\Phi_{\text{ST}} = \Phi_{\text{DPE}}^T = 0.68$.

4.5. Rate constant of α -cleavage of singlet DBK

Let us now assume a 20% limit of α -cleavage in the S_1 state and test for its reasonableness as an upper limit by reference to our measurements and other data in the literature. First, let us estimate the rate constant for α -cleavage from S_1 . The rate of deactivation of S_1 has been measured to be $4.9 \times 10^8 \text{ s}^{-1}$ by picosecond laser spectroscopy [10]. For Scheme 1 the decay rate constant of the excited singlet state of DBK is equal to the sum of the rate constants $k_\alpha^S + k_{\text{ST}} + k_{\text{IC}}$. Since we have calculated above that the partitioning of singlet α -cleavage and ISC is 0.16 to 0.68 (the absolute quantum yields for α -cleavage and ISC respectively), we compute that k_α^S is $0.16 \times (4.9 \times 10^8 \text{ s}^{-1}) = 0.78 \times 10^8 \text{ s}^{-1}$. This value can be compared with the value of $1.0 \times 10^{10} \text{ s}^{-1}$ for α -cleavage in T_1 determined by quenching experiments. Since, as discussed in Section 1, it has been well established [2, 4] that the α -cleavage from T_1 can be 100 times greater than that from S_1 for alkyl ketones, the estimated rate of α -cleavage is completely consistent with this, but it is not convincing because only a qualitative evaluation is possible.

The rate of ISC for DBK is computed to be $k_{\text{ST}} = 0.68 \times (4.9 \times 10^8) = 3.3 \times 10^8 \text{ s}^{-1}$. The rate of ISC for acetone is known to be about $5 \times 10^8 \text{ s}^{-1}$ [17]. The computed value for the rate of ISC of DBK is thus slightly smaller than that for acetone, which might appear to be consistent with the higher fluorescence quantum yield for DBK and with the known decrease in the ISC rate of alkyl ketones by methyl substitution of hydrogens in close vicinity to the carbonyl group [19]. However, analysis of the UV spectra of DBK and its derivatives (Table 1) shows that the maximum extinction coefficient of the n,π^* band is generally ten times that for acetone. Thus it is expected that the radiative rate constant of fluorescence k_f should be about ten

times larger for DBK than for acetone [22, 23]. Thus if the rate constant of ISC for DBK follows the trend for alkyl-substituted acetones, and decreases relative to acetone, the quantum yield of fluorescence of DBK should be more than ten times larger than that of acetone. However, the relative fluorescence quantum yield of DBK is only six times that of acetone, suggesting that the singlet state of DBK possesses at least one deactivation mode that is not available to acetone, which crosses to its triplet state with near unit efficiency. We conclude that, in addition to ISC, there are two deactivation modes accessible to the S_1 state of DBK: singlet α -cleavage and internal conversion to the ground state.

4.6. Singlet photochemistry of *o*-tolyl derivatives of DBK

An analysis of the relationship between structure and relative quantum yields is potentially relevant to the issue of the reasonableness of the conclusions concerning the value of ϕ_r^{ST}/ϕ_r^{OS} and the photochemistry of the S_1 state of DBK and its derivatives. First, we recognize that the quantum yield of fluorescence is low in all cases, so that the radiationless processes of the reaction, internal conversion to S_0 or ISC to T_1 , must dominate the deactivation of S_1 .

Replacement of a phenyl group with an *o*-tolyl group (TBK and MBK) results in significant decreases in the quantum yield of fluorescence, indicating the onset of a competitive radiationless pathway; at the same time, the quantum yield of α -cleavage decreases significantly. *A priori*, we consider that new photochemistry (α -cleavage and δ -hydrogen-atom abstraction) or more efficient radiationless processes (ISC and internal conversion) may account for these observations.

Of the radiationless possibilities (internal conversion, ISC or reaction), we immediately reject ISC because the related *p*-methyl DBK (5) exhibits a higher fluorescence yield (1.06) and quantum yield of DPEs (1.08) compared with TBK and MBK (see Table 2, all values relative to DBK); it seems unlikely that the simple attachment of a methyl group in the ortho position would provide a strong new pathway for inducing ISC. Internal conversion is a possible mechanism for the decrease in the quantum yields of fluorescence and reaction products if a new pathway for deactivating the S_1 state to S_0 is introduced by the introduction of an *o*-tolyl group. Two possible mechanisms of this process are charge transfer quenching and δ -hydrogen-atom-assisted internal conversion. We reject the charge transfer possibility since compound

5 shows a quantum yield of fluorescence comparable with that of DBK and therefore does not display any special pathways for deactivation of S_1 . Thus we conclude that, if enhanced internal conversion is responsible for the reduced fluorescence and product quantum yields, δ -hydrogen-atom interaction with the excited carbonyl group is involved in inducing internal conversion.

Of the two photochemical processes (α -cleavage and δ -hydrogen-atom abstraction) which might be enhanced by methyl substitution, we reject the cleavage process because the change from benzyl to tolyl is known to have only a small effect on the rate constant of α -cleavage [24, 26]. This leaves δ -hydrogen-atom abstraction as the prime photochemical candidate that could explain the results. That at least some of the deactivation is due to reaction is shown by the appearance of an indanole product via δ -hydrogen-atom abstraction, formed exclusively from S_1 , for each of the ketones possessing an *o*-tolyl group. From the working hypothesis that the new deactivation of S_1 is due to δ -hydrogen-atom abstraction, we can compute the rate constant and efficiency of this photochemical process and compare the computed value with those in the literature to establish the validity of this hypothesis.

Based on eqns. (1)–(4), the value for δ -hydrogen-atom abstraction for TBK is calculated to be approximately $1.0 \times 10^9 \text{ s}^{-1}$. This value can be compared with the experimental value for δ -hydrogen-atom abstraction for triplet α -(*o*-tolyl)acetophenone, which is equal to $1.6 \times 10^8 \text{ s}^{-1}$ [26]. Since type II intramolecular hydrogen-atom abstraction is known to occur at a rate of approximately an order of magnitude faster in S_1 than in T_1 [1b, 2], the absolute value calculated by our working hypothesis is reasonable. It is also interesting to note that in *tert*-butyl alkyl ketones, which undergo both α -cleavage and intramolecular hydrogen-atom abstraction, the type II reaction has been reported to occur only in the S_1 state [28].

The interaction of the δ -hydrogen atom with the $S_1(n, \pi^*)$ state of TBK causes a surface crossing with the ground state (S_0) energy surface as the interaction proceeds. As the benzylic C–H bond is stretched, the representative point may proceed to the crossing point and internally convert to the ground state or may proceed completely to the singlet 1,5-biradical via a full δ -hydrogen-atom abstraction [4]. In the case of internal conversion the inefficiency is clearly related to a photophysical radiationless process, but in the case of the abstraction we must postulate an inefficient formation

of the product from the 1,5-biradical, *i.e.* the representative point proceeds along a different reaction coordinate to S_0 as suggested by theory [4]. In searching for analogies to which we may refer to determine whether the photophysical or photochemical pathways (or both) are relevant, we note that the triplet 1,5-biradicals produced in the photolysis of α -(*o*-tolyl)acetophenones undergo extremely efficient cyclization to indanoles [26]. Since these triplet biradicals must intersystem cross to singlet biradicals before cyclization can occur, we expect that the singlet 1,5-biradicals produced from the photolysis of 2–4 also proceed efficiently to products and should not have a high tendency to revert to the starting material in competition with cyclization to indanoles. We find some support for this conclusion in a comparison of the relative values of the rate constants of δ -hydrogen-atom abstraction found for α -(*o*-tolyl)acetophenone and α -mesitylacetophenone ($1.6 \times 10^8 \text{ s}^{-1}$ and $5.5 \times 10^8 \text{ s}^{-1}$ respectively [26], for a ratio of 1/3.4) with the relative values of the absolute quantum yield for indanole formation found for 2 and 4 (0.023 and 0.083 respectively, for a ratio of 1/3.6). The relative fluorescence quantum yields suggest a much higher degree of deactivation of S_1 than can be accounted for by the yield of indanole. Since we have concluded above that the δ -hydrogen-atom interaction is responsible for the deactivation of S_1 and that the singlet biradical produced by full abstraction should proceed efficiently to indanole, we suggest that δ -hydrogen-atom-promoted internal conversion is a major source of deactivation of the S_1 states of 2–4. We can quantitatively estimate the “degree of inefficiency” of intramolecular δ -hydrogen-atom abstraction in TBK from the reaction quantum yield data. Although the difference in the absolute quantum yield of α -cleavage between DBK and TBK is 0.55, the quantum yield of indanole formation in TBK is only 0.023. Since the formation of indanole is the only difference between the photochemistry of DBK and TBK, we should conclude that the formation of indanole from the S_1 state of TBK proceeds with about 4% efficiency.

Since the UV spectral characteristics for DBK and its derivatives are very similar, the rate constants of fluorescence k_F of all of these ketones are expected to be similar [22, 23]. The relative fluorescence quantum yield of 3 is 0.16 that of DBK; for 4, it is 0.05. Yet the α -cleavage efficiencies for these two compounds are 0.26 and 0.13 of that measured for DBK respectively (see Table 2). If α -cleavage only occurred from the triplet state, the addition of an intramolecular hydrogen-

atom abstraction pathway from the singlet state would presumably lessen the fluorescence and α -cleavage yields to the same extent [22]. This conclusion assumes that the rate of α -cleavage from the triplet is limited by the rate of ISC, *i.e.* that methylation on the aryl ring does not affect this rate substantially.

5. Conclusions

The fitting of a master Stern–Volmer equation for the simultaneous quenching of the S_1 and T_1 states of DBK and TBK, a comparison of the fluorescence and α -cleavage quantum yields of DBK and TBK and the CIDNP results of TBK have led to the conclusion that both ketones undergo α -cleavage, the singlet to a lesser (20%–30%) extent than the triplet (70%–80%).

The introduction of a methyl group on the ortho position of the phenyl ring produces another singlet reaction, δ -hydrogen-atom abstraction. This reaction is faster than α -cleavage in S_1 , but does not proceed with high quantum efficiency. A related photophysical process, δ -hydrogen-atom-induced internal conversion, is proposed to be a major mechanism for deactivation of S_1 . This deactivation of S_1 serves to reduce ISC and competes effectively with α -cleavage in S_1 , and thus a decrease in the quantum yield of α -cleavage is observed.

From the fluorescence quantum yield and the quantum yields of α -cleavage and formation of indanole, a mechanism can be qualitatively postulated (Scheme 2). For TBK, 3 and MBK, which show fast singlet hydrogen-atom abstraction, the quantum yields of fluorescence and α -cleavage decrease.

The photochemistry of DBK and its derivatives thus demonstrates both singlet and triplet chemistry in analogy with other dialkyl ketones. The results of this investigation require a quantitative (addition of singlet state photochemistry) but not a qualitative change of the paradigm of the photolysis of DBK (Scheme 1).

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DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	20